

THE KINETICS OF THE OXIDATION OF
HYPOPHOSPHITE BY PERRUTHENATE
IN AQUEOUS ALKALI

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SAMUEL J. PATON
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This is to certify that the
thesis entitled

THE KINETICS OF THE OXIDATION OF HYPOPHOSPHITE BY
PERRUTHENATE IN AQUEOUS ALKALI

presented by

Samuel J. Paton

has been accepted towards fulfillment
of the requirements for

Ph.D. degree in Chemistry

A handwritten signature in dark ink, appearing to read "Carl H. Bamberg".

Major professor

Date October 13, 1972

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ABSTRACT

THE KINETICS OF THE OXIDATION OF HYPOPHOSPHITE BY PERRUTHENATE IN AQUEOUS ALKALI

The kinetics of the oxidation of hypophosphite by perruthenate was studied at various temperatures in 0.300 M KOH. The change in perruthenate concentration was followed spectrophotometrically under pseudo first order (stopped-flow) and second order conditions. Data were analyzed by a curve fitting computer program. The reaction is first order with respect to each anion and hydroxide with a rate constant of $248 \text{ M}^{-2}\text{sec}^{-1}$ at 24.8° . The rate decreases linearly with decreasing pH. The Arrhenius activation energy E_a is 2.46 kcal/mole and the entropy of activation $\Delta S^{\ddagger} = -41.3 \text{ eu}$. Results are compared to published studies of hypophosphorus acid in acidic solution and hypophosphite anion in basic solution. The proposed mechanism involves an equilibrium with hydroxide ion and hypophosphite. The activated complex is probably a hydroxide bridged species of hypophosphite and perruthenate.

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BY PERRUTHENATE IN AQUEOUS ALKALI

By

Samuel J. Paton

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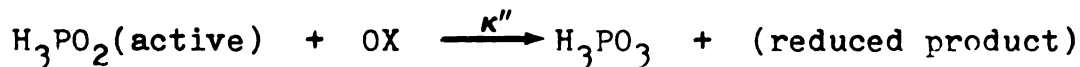
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INTRODUCTION

P. L. Dulong, in 1816, treated phosphides of alkaline earths with water, isolated hypophosphite salts, and proposed the name hypophosphorous acid.¹ Since then the mono protic acid and many of its salts have been studied. Detailed studies of the kinetics of reactions involving H_3PO_2 as a reducing agent began with Mitchell.² He suggested an acid catalyzed equilibrium between H_3PO_2 and an active form of the acid



which was immediately oxidized.



The general form of the rate law,

$$-\frac{d(\text{H}_3\text{PO}_2)}{dt} = \frac{k(\text{H}_3\text{PO}_2)(\text{H}^+)}{1 + \frac{k'(\text{H}^+)}{k''(\text{OX})}}$$

is obeyed for the following oxidants: I_2 , Br_2 , Cl_2 , IO_3^- , HCrO_4^- , $\text{Ce}(\text{IV})$, and $\text{Tl}(\text{III})$ (References 2 through 7, respectively). Evidence for complex formation between H_3PO_2 and the oxidant was presented in the latter two studies. Isotope exchange studies by Jenkins and Yost⁸ (T/H) and Fratiello and Anderson⁹ (D/H) further substantiated

the inactive/active phenomena for H_3PO_2 . Other rate laws (involving complex formation as well as the inactive/active concept) were observed by Carroll and Thomas¹⁰ (Ce(IV)), Cooper et. al.¹¹ (V(V)), and Cooper¹² (Cr(VI)). All of these studies were in acidic or neutral solutions. Studies of reactions of hypophosphite in basic solutions are limited. In 1912, Sieverts and Loessner¹³ studied the rate of the decomposition reaction at 91° and 100° in 1-4 M NaOH solution. Their data conformed to the rate equation

$$-\frac{d(\text{H}_2\text{PO}_2^-)}{dt} = k(\text{H}_2\text{PO}_2^-)(\text{OH}^-)^2$$

and they observed a "normal temperature dependence". Jenkins and Yost⁸ mentioned decomposition problems in their work at high pH. Roper, Haas and Gillman¹⁴ published results of a proton nmr study on the base catalyzed hydrogen-deuterium exchange on hypophosphite anion (discussed in detail under RESULTS). The authors suggest the rate of production of the reactive intermediate was observed. Ben-Zvi¹⁵ studied a free radical chain mechanism of oxidation by peroxydisulphate up to pH=11. No other basic solution studies have been published.

This study was intended to observe effects of a reactive intermediate of hypophosphite in basic solution. It was necessary to use an oxidant known to gain electrons rapidly. Luoma¹⁶ demonstrated the extremely rapid exchange between RuO_4^- and $\text{RuO}_4^=$ as well as a fast reaction between RuO_4^- and $\text{MnO}_4^=$. Thus, the choice of KRuO_4 as the oxidizing agent is reasonable.

EXPERIMENTAL

A. PREPARATION AND ANALYSIS OF REAGENTS KH_2PO_2

About 400 g of Baker and Adamson KH_2PO_2 was added to 300 ml of distilled water, and heated to 50° to facilitate dissolution. The warm solution darkened. The grey matter was removed by filtering through medium porosity filter paper. The clear solution was cooled to 7° in a refrigerator but no crystals appeared. The solution was transferred to a Rotovap (®) and maintained at 30° by means of a water bath and the apparatus was evacuated to about 10 torr. Crystals of KH_2PO_2 formed suddenly and were removed by filtration on a coarse frit. After several washings with distilled water, the white crystals (200 g) were stored in a brown bottle. The supernatant was returned to the Rotovap (®) evaporator for

second (50 g) and third (20 g) batches of crystals. The three samples of KH_2PO_2 were dried in vacuo over Drierite [®] for several hours, then exposed to the air overnight. Two samples from each of the three crystallizations were analyzed by the method of Ogawa.¹⁷ The determined molecular weight ranged from 104.50 to 105.93 with an average of 105.05 g/mole (actual molecular weight = 104.09 g/mole). The three batches of the salt were crushed and thoroughly mixed. Four samples of about 0.1 g each were analyzed by the two part method of Jones and Swift.¹⁸ The first part, a sensitive analysis for phosphite (the most likely contaminant), showed none was present. From the second part, the oxidation of all P(I) and P(III) compounds to phosphate, the determined molecular weight was 105.07 ± 10 g/mole. Galbraith Laboratories found 29.50% P which corresponds to 105.0 g/mole. Actual %P for KH_2PO_2 is 29.76%. The value of 105.06 for the molecular weight of KH_2PO_2 was used for all future calculations. The 0.9% difference was attributed to water adsorbed on the surface of the crystals. The assumed molecular weight was confirmed several times by the method of Jones and Swift during the course of the study.

KRuO₄

Ruthenium metal powder (99.9%) from K&K Laboratories and anhydrous RuCl₃ (99.9%) from Alfa Inorganics were the sources of ruthenium. The starting material KRuO₄ was prepared in the following manner. Ten g of sodium peroxide and three g of Ru powder were fused in a nickel crucible over a Meeker burner. After cooling, the fused mass was dissolved in 300 ml of distilled water. The solution was carefully acidified with 6 M HCl, which caused the orange solution (mostly RuO₄⁼) to turn black (due to the formation of hydrated Ru(IV) oxide). The pH was adjusted to 7 with NaHCO₃. Hydrated oxide was removed by filtration on a medium frit, dried at 110°, and ground into a powder. (After each experiment Ru was precipitated as the oxide and recycled at this point.) The black powder was evaporated to dryness with concentrated HCl. The water soluble RuCl₃ product (which contained a small amount of the hydrated oxide) was the starting material for the preparation of RuO₄. The volatile tetraoxide was generated according to the recipe of Larsen and Ross.¹⁹ A typical preparation was carried out in a one liter, three neck (24/40) round

bottom flask. An overhead stirring assembly was placed in the central neck. A 7 mm glass tube for N_2 flow in a 24/25 Teflon (®) adapter (RuO_4 reacts quickly with all stopcock grease, and even discolors Teflon (®) was placed in another neck. The third neck contained another 24/25 adapter which had a U-shaped tube (10 x 25 x 10 cm). This tube delivered RuO_4 (under slightly positive pressure of N_2) into a 100 ml flask equipped with a side arm. The receiving vessel was submerged in an isopropanol/dry-ice bath. Reagents used were 3.5 g of " $RuCl_3$ ", 125 g $NaBiO_3$, 500 ml 6N H_2SO_4 , and 200 ml of distilled water. As the mixture was stirred, N_2 was bubbled through at 3 to 5 bubbles per second. Heat was applied from a heating mantle to bring the mixture to a temperature near 90° . By this time bright yellow RuO_4 (as well as ice) was observed in the receiving flask. When RuO_4 no longer condensed in the delivery tube, the reaction was judged completed. The contents of the receiving vessel were quickly added to an equal volume of 0.3 M KOH solution (total volume 80 ml) in a large weighing bottle. The top was replaced and the weighing bottle placed in a refrigerator at 7° for 3 days. At 12

hour intervals, 3 ml of saturated KCl solution were added.

The shiny black crystals of KRuO_4 were removed from the orange supernatant on a coarse filter frit. After being washed four times with small amounts of distilled water the KRuO_4 (.3 g) was dried and stored over Drierite (R) .

(Calculated for KRuO_4 : Ru, 49.50. Found = 49.77) The actual RuO_4^- and $\text{RuO}_4^{=}$ concentrations were calculated from absorbances at 465 and 383.5 nm by use of molar absorptivities given by Luoma.¹⁶ (Total Ru concentration was consistently 2-3% lower than the value calculated from the weighed amount of KRuO_4 .)

KOH

The reaction medium of 0.3 M KOH was prepared fresh for each experiment from Baker's Analyzed Reagent (R) which contained less than 0.8% carbonate. Sufficient pellets to give slightly more than a 0.3 M solution were dissolved in distilled water (deionized water distilled from KMnO_4 and then from itself). From this solution exactly 100 ml were removed and used to titrate weighed samples of potassium hydrogen phthalate to the phenolphthalien endpoint. Distilled water was added to dilute the stock to exactly

0.300 M in KOH. All other reagents met ACS standards and were used as taken from their containers.

B. SECOND ORDER KINETICS

When RuO_4^- and H_2PO_2^- concentrations were similar and near 2×10^{-4} molar, the reaction time was of the order of minutes. A Cary Model 14 spectrophotometer was used for monitoring the concentration of RuO_4^- or $\text{RuO}_4^=$ as a function of time. A typical experiment began with the calibration of 5 cm cells made of Pyrex (silica seemed to affect the stability of RuO_4^-) at both 465 nm and 383.5 nm (the adsorption maxima for $\text{RuO}_4^=$ and RuO_4^- , respectively).

A stock solution of 0.300 M KOH was prepared as described previously. A 0.131 g sample of KH_2PO_2 was dissolved in the hydroxide and the solution diluted to 250 ml. From this solution, 25.0 ml was pipetted into another 250 ml volumetric flask and again diluted to the mark with KOH. The resulting solution was 5.00×10^{-4} M in KH_2PO_2 .

A 500 ml volumetric flask was partially filled with 300 ml of the stock 0.300 M KOH. The stock solution of KRuO_4 was prepared by weighing 0.0451 g of KRuO_4 into the flask and quickly swirling the contents. (It was found

that KRuO_4 crystals caught along the walls and rapidly decomposed to RuO_4^- unless quickly brought into solution.) The resulting solution was $4.42 \times 10^{-4} \text{ M}$ in KRuO_4 .

The three stock solutions (KOH , KRuO_4 , and KH_2PO_2) were stored in a controlled temperature water bath. (Water from this heat sink was pumped through the cooling passages of the cell compartments of the Cary 14). Aliquots (25.0 ml) of the hypophosphite and perruthenate were pipetted into separate 100 ml beakers which were held in the bath. The beakers were removed and the perruthenate solution was quickly poured into the hypophosphite solution. (This action was $t = 0.0 \text{ sec}$ and a timer was started.) The mixture was poured between the beakers four times, the sample cell was rinsed twice, filled, and placed in the sample chamber. The recording pen was actuated immediately (about $t = 25 \text{ sec}$) and the chart paper started at $t = 30 \text{ sec}$. The absorbance was recorded at 465 nm until at least 90% of the RuO_4^- was converted to RuO_4^- . Absorbance readings at 383.5 nm were recorded at several times during the course of the reaction. The experiment was repeated several times alternating hydroxide with hypophosphite.

TREATMENT OF DATA

Absorbance was read from the chart at minimum of 15 different times which were selected such that half were in the first quarter of the reaction (where $\Delta A/\Delta t$ was greatest). An average value for total $\text{RuO}_4^- + \text{RuO}_4^=$ concentration was determined from the absorbances at 383.5 and 465 nm. With this value and an absorbance, the perruthenate concentration at any time "t" could be calculated. A small correction factor (20) to account for oxidizable contaminants in the KOH pellets was applied to the value of RuO_4^- concentration. The value thus obtained represented the concentration of RuO_4^- that had not yet reacted with H_2PO_2^- . This variable was fitted to a rate law as described under "Results".

C. PSEUDO FIRST ORDER KINETICS

Two different stopped-flow apparatus made it possible to study the reaction over a wide range of concentrations. One of the home-built instruments delivered about 15 ml of each reactant solution into a mixing chamber. The flow continued through 2 mm capillary tubing to a solenoid stop valve and then to a catch vessel. A beam of

light from a monochomator passed through the 2 mm tubing perpendicular to the flow of liquid and then into a photomultiplier. The amplified output voltage (directly proportional to %T) was logarithmically converted and stored on a recording oscilloscope. Voltage (now proportional to absorbance) versus time traces were photographed with Polaroid ® film. Treatment of these data is described later.

The other stopped-flow instrument²¹ was basically similar except for light path length. Each syringe pushed about 1 ml through a mixing chamber into an observation cell of 2 mm stainless steel tubing 2 cm long. Light traversed the length of the cell, thus giving a path length 10 times the system previously described. Although the two instruments exhibited major detailed differences, the principles of operation were identical.

In a typical experiment (on either instrument), the oscilloscope recorded a trace representing zero absorbance (0.300 M KOH in each syringe) at 465 nm. The RuO_4^- solution was admitted to one syringe and the trace corresponding to the absorbance of RuO_4^- only was recorded.

These traces were photographed, and were the basis for all absorbance assignments. The other syringe was loaded with H_2PO_2^- and the reaction trace was recorded and photographed. After a thorough rinsing, the entire procedure was repeated with solutions of different concentrations. Several reactions (traces) were recorded and photographed at each concentration.

TREATMENT OF DATA

The grid pattern of the photograph of the oscilloscope was scaled for absorbance and time. Absorbance was converted to RuO_4^- concentration. The absorbance value at $t = 0.0$ sec was scaled to 1.00 and all other concentrations divided by that value. Concentration versus time was plotted on semi-log paper, and the half-life for each reaction estimated from the graph.

D. VARIATION IN TEMPERATURE

A 100 l. water bath equipped with circulating pump, tap water cooling coils, and thermostatically controlled heating blades provided a constant temperature of 24.8° for the cell compartment of the Cary 14. The temperature of the solution in the 5 cm cell in the sample compartment

was always within 0.1° of that value. A 50 l. coolant bath unit manufactured by the Wilkens-Anderson Company was used to control temperature above or below ambient conditions. A thermometer was inserted into the 5 cm cell at the end of each reaction to measure the actual temperature. Data were treated as described previously.

E. VARIATION OF pH

Potassium hydroxide pellets and K_3PO_4 were mixed in various proportions to vary the pH while maintaining the ionic strength (on a molar scale) at 0.30. A Corning Model 10 pH meter equipped with a general purpose glass electrode and a new reference electrode indicated the actual pH of the various solutions. Measurements before and after the reaction differed by less than 0.1 pH unit. Data were treated as described previously.

F. PRODUCTS OF THE REACTION

It was clear that perruthenate was converted to ruthenate and that the rate of reduction of RuO_4^- by $H_2PO_2^-$ was not significant at these concentrations and time scales. Indeed, knowledge of the total $RuO_4^- + RuO_4^{2-}$ concentration was an integral part of the data analysis.

Inconclusive results were obtained from the several attempts to establish the nature of the product of the oxidation of hypophosphite. A 50 ml aliquot of 8×10^{-3} M RuO_4^- was allowed to react with a 5 ml aliquot of 5×10^{-2} M H_2PO_2^- . When all ruthenium was in the +6 state, the solution was carefully neutralized with 6 M HCl . A small amount of saturated NaHCO_3 was added to adjust the pH. Hydrated Ru(IV) oxide precipitated as the solution approached neutrality. The solution was centrifuged, and the decanted portion filtered through a medium frit. The phosphite and hypophosphite were determined in the very pale yellow solution by the method of Jones and Swift.¹⁸

Thin layer chromatography identified the only reaction product to be phosphite. The plates were Baker-Flex brand #0-4468 (cellulose). Seiler's²² recommendation for the solvent, a mixture of methanol concd ammonia-10% trichloroacetic acid-water (50+15+5+30), gave excellent results. Substitution of sodium molybdate for ammonium molybdate caused no difficulty. The R_f value for HPO_3^- (compared to H_2PO_2^-) was 0.77 for reference and 0.76 for sample.

No paramagnetic species were observed in the frozen (liquid N₂) reaction solution. Luoma¹⁶ also failed to observe an esr signal from RuO₄⁻. The samples were run on a Varian model E-4 at liquid N₂ temperature and were scanned from 1500 to 6500 Gauss at 9.295 GHZ.

RESULTS

A. THE RATE EQUATION

Extensive stopped-flow studies were designed to observe the effects of an equilibrium between inactive and active forms of H₂PO₂⁻. Table I presents the half-lives for the disappearance of RuO₄⁻ under various psuedo first order conditions. The t_{1/2} values are consistent and all plots are linear for at least two half-lives.

Data from dilute solution studies were analyzed by a curve fitting computer program written by Dye and Nicely.²³

The second order equation

$$\frac{dx}{dt} = k_2(Ru - x)(P - \frac{x}{2}) \quad (1)$$

Table I

Half-Life Values for RuO_4^- Disappearance
Initial Concentration ($\text{M} \times 10^4$)

$[\text{H}_2\text{PO}_2^-]$	RuO_4^-					
	<u>12.3</u>	<u>5.56</u>	<u>4.55</u>	<u>3.52</u>	<u>.745</u>	<u>.73</u>
	$t_{1/2} \text{ (sec)}$					
1000.	.080*	.089		.10	.13	
500.	.18	.17				
250.	.355	.39	.40	.40	.40	.48
125.			.81			.88
50.			2.1			2.2
25.			4.25			4.3
12.5			8.3			8.7
5.0			20.5			19.

* All values in sec. $\pm 10\%$

was integrated and rearranged to the form

$$x = \frac{2Ru(e^{yk_2t} - 1)}{\frac{Ru}{P} e^{yk_2t} - 2} \quad y = \frac{Ru - 2P}{2} \quad (2)$$

where Ru and P represent initial concentrations of RuO_4^- and H_2PO_2^- , k_2 is the second order rate constant, t is time, and x is the extent of reaction (= the concentration of RuO_4^- converted to $\text{RuO}_4^=$ at any time t). The input data are x and time, and k is optimized to give minimum residuals between the input and the calculated x.

Results of these calculations appear in Table II.

Figure I is a computer plot of the input variable and the calculated x vs time for $\text{KH}_2\text{PO}_2 = 2.5 \times 10^{-4} \text{ M}$.

Experimental points (input) are designated with x, o indicates a calculated point, and = means experimental and calculated points differ by less than the experimental uncertainty (usually less than 5%).

The perruthenate concentration can be introduced as a second adjustable parameter in equation (2). The curve-fitting program will then optimize both parameters. Such calculations are listed in Table III and a representative computer plot is Figure II (for $\text{H}_2\text{PO}_2^- = 2.5 \times 10^{-4} \text{ M}$).

Table II

The Rate of the Reaction in 0.300 M KOH at 24.8° C
 Initial Concentrations (M x 10⁴)

$\left[\text{H}_2\text{PO}_2^- \right]$	$\left[\text{RuO}_4^- \right]$	$\overset{k_2}{\text{M}^{-1} \text{ sec}^{-1}}$
2.50	1.72	56.6 $\pm$.4
2.00	1.73	59.1 $\pm$.5
1.50	1.69	59.1 $\pm$.5
1.00	1.69	59.9 $\pm$.9
0.500	1.66	<u>57.8 $\pm$ 1.1</u>
		58.5 $\pm$ 1.8

Figure I
Extent of Reaction vs Time. 24.8°

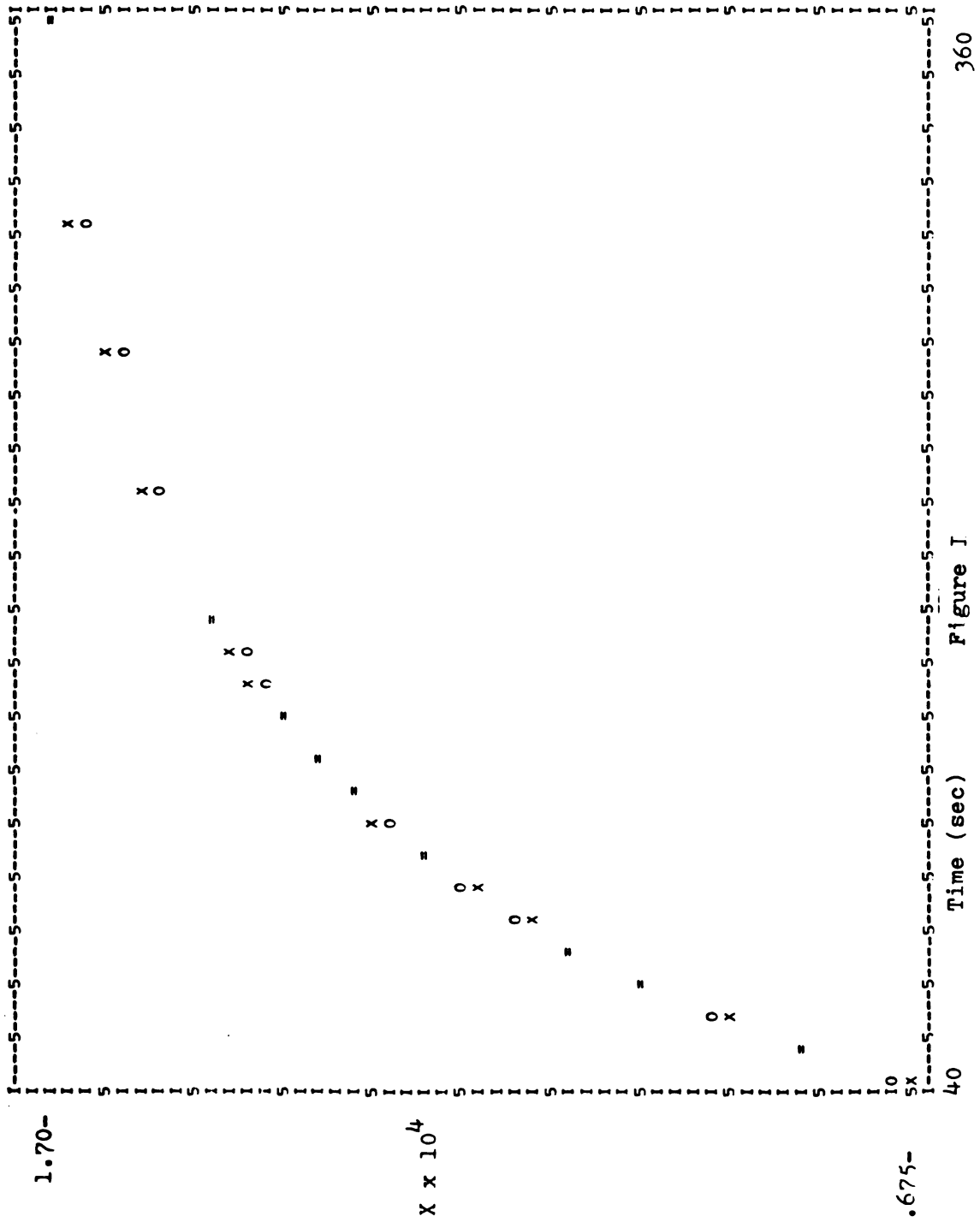


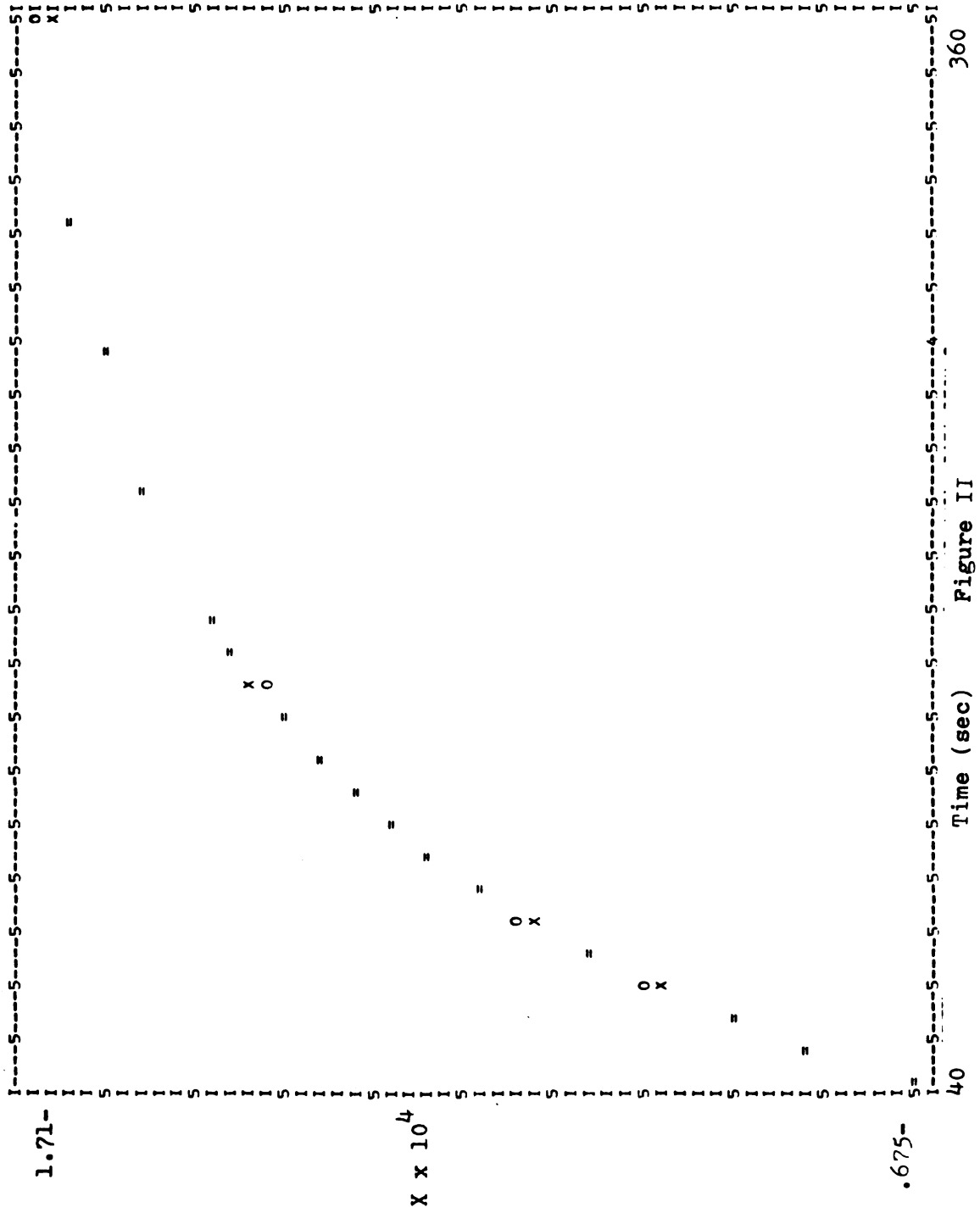
Table III

The Rate in 0.300 M KOH at 24.8°C
 Initial Concentrations (M x 10⁴)

$\left[\text{H}_2\text{PO}_2^- \right]$	$\left[\text{RuO}_4^- \right]$	<u>calculated</u> $\left[\text{RuO}_4^- \right]$	$\frac{k_2}{\text{M}^{-1} \text{ sec}^{-1}}$
2.50	1.72	1.76 $\pm$.01	53.9 $\pm$.4
2.00	1.73	1.71 $\pm$.01	61.6 $\pm$.4
1.50	1.69	1.73 $\pm$.01	56.3 $\pm$.6
1.00	1.69	1.77 $\pm$.01	53.9 $\pm$.6
0.500	1.66	3.28 $\pm$.40	<u>25.6 $\pm$.3</u>
		Avg*	56.4 $\pm$.5

*Exclude last value

Figure II
Extent of Reaction vs Time. 2 Parameters



It was judged desirable to minimize machine manipulations of the data, so all results are calculated from equation (2) with k_2 the only parameter.

B. ACTIVATION PARAMETERS

All temperature studies were carried out in 0.300 M KOH. Results from these reactions are listed in Tables IV, V, VI, and VII. The Arrhenius activation energy E_a , calculated

from

$$k_3 = A e^{-E_a/RT}$$

is 2.46 ± 0.2 kcal/mole and the pre-exponential factor

$A = 1.63 \times 10^5 \text{ M}^{-1} \text{ sec}^{-1}$ (see Figure III). Activation

enthalpy ($\Delta H^\ddagger$) and entropy ($\Delta S^\ddagger$) are found from the equation

where

$$k_2 = \frac{kT}{h} e^{\frac{\Delta S^\ddagger}{R}} e^{-\frac{\Delta H^\ddagger}{RT}}$$

$$\begin{aligned} k_r &= \text{rate of reaction} \\ k &= \text{Boltzman's constant} \\ h &= \text{Planck's constant} \\ R &= \text{gas constant} \\ T &= \text{temperature} \\ \Delta H^\ddagger &= E_a - RT \end{aligned}$$

The activation parameters are $\Delta H^\ddagger = 1.86 \pm 0.2$ kcal/mole

and $\Delta S^\ddagger = -41.3 \pm 7$ eu.

Table IV

The Rate of the Reaction in 0.300 M KOH at 4.3°
 Initial Concentrations (M x 10⁴)

$\left[\text{H}_2\text{PO}_2^- \right]$	$\left[\text{RuO}_4^- \right]$	$\frac{k_2}{\text{M}^{-1} \text{ sec}^{-1}}$
2.49	1.70	43.9 $\pm$.4
1.25	1.77	45.5 $\pm$.6
2.49	1.77	45.3 $\pm$.3
1.25	1.71	43.3 $\pm$ 1.2
		<u>44.5 $\pm$ 1.0</u>

Table V

The Rate of the Reaction in 0.300 M KOH at 14.7°

Initial Concentrations (M x 10⁴)

$\left[\text{H}_2\text{PO}_2^- \right]$	$\left[\text{RuO}_4^- \right]$	$\frac{k_2}{\text{M}^{-1} \text{ sec}^{-1}}$
2.49	1.81	48.5 $\pm$.3
1.25	1.79	54.1 $\pm$.6
2.49	1.79	49.1 $\pm$.4
1.25	1.80	45.1 $\pm$.6
		<u>49.2 $\pm$ 1.0</u>

Table VI

The Rate of the Reaction in 0.300 M KOH at 34.3°

Initial Concentrations (M x 10⁴)

$\left[\text{H}_2\text{PO}_2^- \right]$	$\left[\text{RuO}_4^- \right]$	$\frac{k_2}{\text{M}^{-1} \text{ sec}^{-1}}$
2.53	1.57	64.1 $\pm$.7
1.90	1.56	70.0 $\pm$.7
1.27	1.50	73.1 $\pm$ 1.0
0.633	1.47	66.3 $\pm$ 1.7
		<u>68.4 $\pm$ 2.0</u>

Table VII

The Rate of the Reaction in 0.300 M KOH at 42.8°

Initial Concentrations (M x 10⁴)

$\left[\text{H}_2\text{PO}_2^- \right]$	$\left[\text{RuO}_4^- \right]$	$\frac{k_2}{\text{M}^{-1} \text{ sec}^{-1}}$
2.53	1.65	73.7 $\pm$ 1.0
1.90	1.65	66.3 $\pm$.9
1.27	1.61	84.9 $\pm$ 1.4
2.53	1.45	<u>73.6 $\pm$.6</u>
		74.6 $\pm$ 5.0

Figure III
Plot of Arrhenius Activation Energy Function

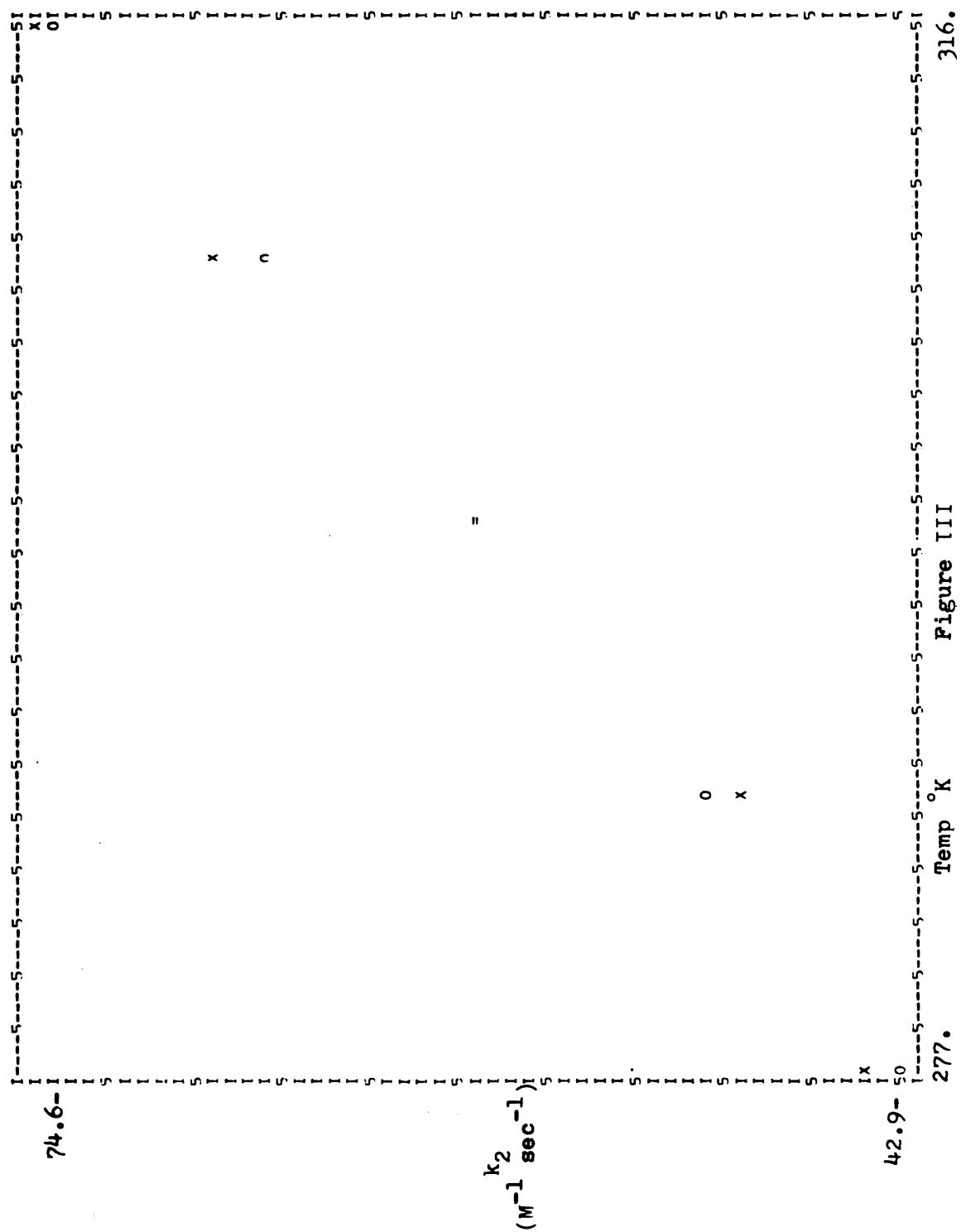


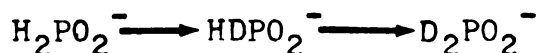
Figure III

C. pH DEPENDENCE

A positive hydroxide ion dependence for the rate constant was expected. Experiments showed a large effect, and therefore the reaction was studied over a wide range of hydroxide concentration. At the lowest pH (10.3), the reaction solution was turbid when removed from the Cary 14. It was obvious other reactions interfered at lower pH. Table VIII presents rate constant results from pH studies. A plot of k_2 vs (OH^-) has a slope of 248 (See Figure IV), which indicates a positive OH^- concentration dependence.

DISCUSSION

Roper, Haas, and Gillman's¹⁴ rate data for the exchange reaction in D_2O



obeyed the rate law

$$\text{rate} = k(OD^-)(H_2PO_2^-) \quad (3)$$

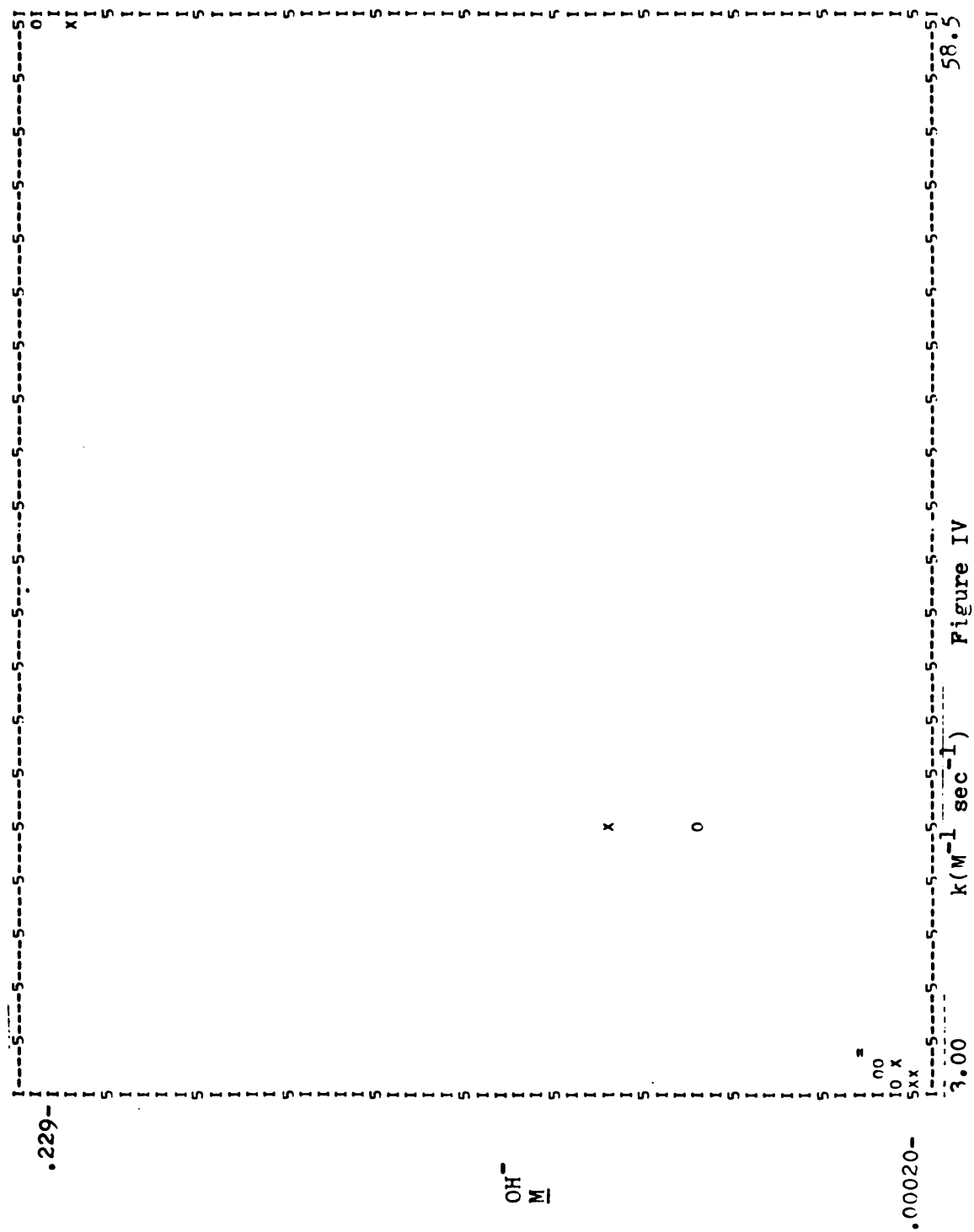
with $k = 3 \times 10^{-3} \text{ M}^{-1}\text{sec}^{-1}$ at 25°C . They concluded

Table VIII

Dependence of the Rate on $[\text{OH}^-]$ at 24.8°
 Initial Concentration ($\text{M} \times 10^4$)

$[\text{H}_2\text{PO}_2^-]$	$[\text{RuO}_4^-]$	$\frac{[\text{OH}^-]}{\text{mole/liter.}}$	$\frac{k_2}{\text{M}^{-1} \text{ sec}^{-1}}$
2.64	2.76	0.0833	$16.5 \pm .1$
3.08	1.98	0.0158	$5.15 \pm .09$
2.58	2.89	0.00851	$4.17 \pm .03$
3.49	2.55	0.00363	$3.78 \pm .07$
2.53	2.28	0.000200	$3.00 \pm .05$

Figure IV
Dependence of the Rate on $[\text{OH}^-]$



"....we believe it (the rate controlling step) to correspond to the removal of a hydrogen from the hypophosphite anion to form a triply connected phosphorous dianion, HPO_2^{2-} , viz., $\text{H}_2\text{PO}_2^- + \text{OD}^- \longrightarrow \text{HPO}_2^{2-} + \text{HDO}$. This reactive species then will pick up an additional hydrogen or deuterium atom from the solvent in a rapid step: $\text{HPO}_2^{2-} + \text{D}_2\text{O} \longrightarrow \text{HDPO}_2^- + \text{OD}^-$. If this view is correct, the rate to which equation (3) refers is actually the rate of production of the reactive intermediate."

If this reactive intermediate is the species proposed by Mitchell² (i.e., the form that is readily oxidized), then it should be easily oxidized by the strong oxidant RuO_4^- . If the reactive intermediate concentration is substantially less than the inactive form (say 10%), the reaction should clearly deviate from pseudo-first order kinetics before the initial H_2PO_2^- to RuO_4^- ratio is below 20:1. The $t_{1/2}$ values in Table I do not deviate from the expected pattern. Therefore, the reactive species is at least 10% of (and quite likely equal to) the H_2PO_2^- concentration at all times during the reaction.

When the ratio of H_2PO_2^- to RuO_4^- is near unity, the reaction data conform to the second order expression

$$\frac{dx}{dt} = k_2(\text{Ru} - x)(\text{P} - \frac{x}{2})$$

with $k = 58.5 \text{ M}^{-1} \text{ sec}^{-1}$ at 25°C . Stopped flow data fitted to equation (2), treated as described previously, gives similar values for the second order rate constant k_2 (see Table IX). In order to test for a contribution to the rate expression from a OH^- concentration term, the equation

$$\frac{dx}{dt} = (k_2 + k_3(\text{OH}^-))(\text{Ru} - x)(\text{P} - \frac{x}{2})$$

was tested. A plot of k_2 (the observed k) vs (OH^-) has a slope of $248. \pm 14.$ and an intercept of $0.2 \pm 1.8.$ The hydroxide ion dependence in the rate law must be first order, and k_2 is zero within experimental error. The overall rate law is

$$\frac{dx}{dt} = k_3(\text{Ru} - x)(\text{P} - \frac{x}{2})(\text{OH}^-)$$

with $k_3 = 248. \pm 14 \text{ M}^{-2} \text{ sec}^{-1}$ when OH^- is in excess.

A. G. Miroshnichenko and V. A. Luneok-Burmakina²⁴ published the results of the oxidation of H_3PO_2 by H_2O_2 in acid solution. Although their conclusions appear self contradictory, they do claim (from ^{18}O studies) that peroxide rather than water is the source of oxygen in the formation of phosphite. In this study, OH^- or water must

Table IX

Representative Stopped - Flow Data

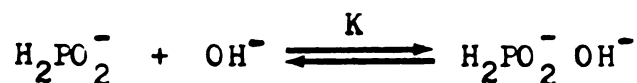
Initial Concentration ($\underline{M} \times 10^4$)

$\underline{[H_2PO_2^-]}$	calc $\underline{[RuO_4^-]}$	$\underline{M^{-1} \text{ } ^k_2 \text{ sec}^{-1}}$
1000.	12.6 $\pm$.5	76.5 $\pm$ 5.8
500.	6.03 $\pm$.2	66.6 $\pm$ 4.3
125.	4.56 $\pm$.02	71.4 $\pm$ 1.2
25.	4.58 $\pm$.04	72.4 $\pm$ 1.6
5.	4.86 $\pm$.03	<u>76.8 $\pm$.7</u>
		72.7 $\pm$ 4.0

be the source of oxygen, since the exchange of O between H_2O and RuO_4^- is slow compared to the time scale of the present reaction.²⁶

Ben-Zvi¹⁵ proposed the formation of a hypophosphite radical in the oxidation by peroxydisulphate. He listed the activation energy of the formation of the radical as 6.6 kcal/mole. The rate equation is not simple and the observed rate constant decreased to a plateau (about $10^{-3} \text{ M}^{-\frac{1}{2}} \text{ sec}^{-1}$) at pH = 11. Although a free radical chain mechanism for oxidation by RuO_4^- cannot be excluded, it could not be substantiated, and the data conform well to the second order rate law.

Roper, Haas, and Gillman¹⁴ report an E_a of about 19 kcal/mole which is similar to activation energies from other studies on the oxidation of hypophosphite. The low E_a from this study (2.5 kcal/mole) and the large entropy of activation (-41 eu) indicates the rate determining step is other than the inactive/active tautomerism. The data can be explained by a pre-equilibrium between H_2PO_2^- and OH^-



The large, negative activation entropy indicates oxidation of H_2PO_2^- occurs by means of a bridged activated complex. The bridge probably involves OH^- ion. The rate expression indicates one RuO_4^- ion is involved in the rate determining step. This suggests that a P(II) species may have a transient existence.

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BIBLIOGRAPHY

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APPENDIX A

APPENDIX A

Consider the rate equation

$$\frac{dx}{dt} = k_2 \left(Ru - x \right) \left(P - \frac{x}{2} \right) \quad (1)$$

where Ru and P represent initial concentrations of RuO_4^- and $H_2PO_2^-$, respectively. The variable x corresponds to the decrease in RuO_4^- concentration (or increase in $RuO_4^=$ concentration) due to the reaction with $H_2PO_2^-$. Data are RuO_4^- concentration and time. Blank experiments (without $H_2PO_2^-$) indicate reduction of RuO_4^- (attributed to contamination of KOH pellets). Thus, when $H_2PO_2^-$ is added to RuO_4^- solution, the production of $RuO_4^=$ is from two sources, and x in equation (1) cannot be identified as the observed increase in $RuO_4^=$ concentration. Clearly, x must be a value slightly less than the observed increase in $RuO_4^=$ concentration at each time t. In Figure A-1, curve 1 is the case when RuO_4^- is not reduced in a blank experiment and curve 2 represents reduction of RuO_4^- in a blank. Curve 5 is the observed reduction of RuO_4^- due to $H_2PO_2^-$ and contamination. Curve 3 is curve 5 plus curve 2. The reduction of RuO_4^- due to $H_2PO_2^-$ is represented by curve 4, which must lie between curves 3 and 5. The variable x at any time t is the value of curve 4 minus the value of curve 1. The problem is how to calculate curve 4.

Figure A-1

Extent of Reaction vs Time, Hypothetical

iii

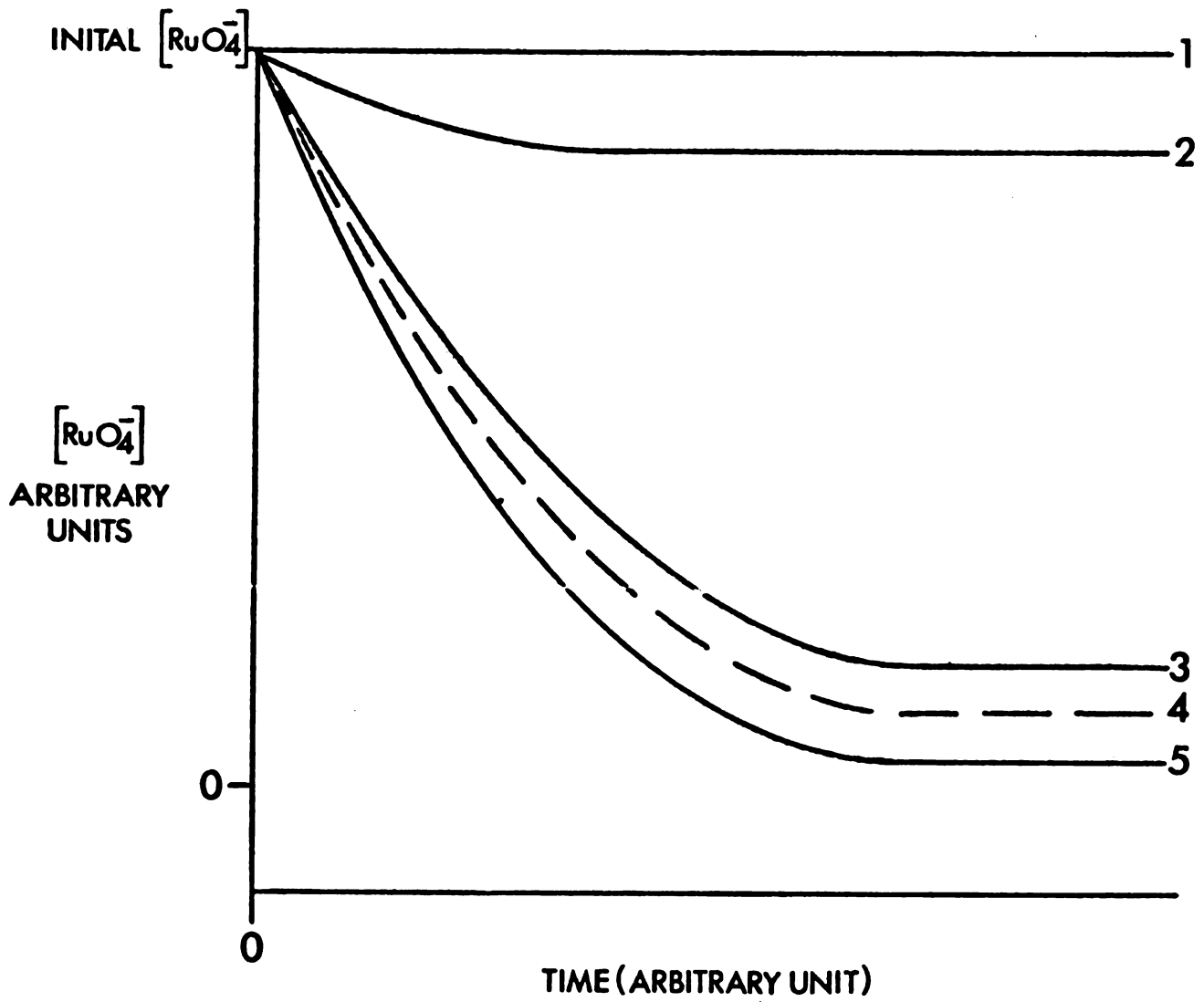


FIGURE
A-1

APPENDIX A (cont'd)

Ideally, the reduction of RuO_4^- due to the contamination would be treated as a concurrent reaction and the individual rate expressions combined into a comprehensive rate law. Without knowledge of the nature of the contamination or its concentration, such a mathematical expression is difficult to justify (i.e., the stoichiometry).

It is reasonable to assume that, in curve 5, the contribution due to contamination can be related to curve 2. If, at time t , the blank experiment reveals that 5% of the initial RuO_4^- has been reduced to $\text{RuO}_4^=$, then 5% of the observed decrease in RuO_4^- concentration in curve 5 is due to the contamination. Thus, dividing the observed RuO_4^- on curve 5 by 0.95 produces a new RuO_4^- concentration at time t . Subtracting this RuO_4^- concentration from curve 1 (the initial RuO_4^- concentration) gives the change in RuO_4^- concentration due to the reaction with H_2PO_2^- . This value is x in equation (1).

The data were selected from experiments at 14.7° in 0.300 M KOH with H_2PO_2^- concentration of $2.49 \times 10^{-4} \text{ M}$ (Table V). In the first experiment 20.0 ml of RuO_4^- solution was added to 20.0 ml of 0.300 M KOH (Table A-1).

Table A-1

Absorbance at 14.7°C, Experiment 1

Time (sec)	Absorbance (383.5 nm) 465.0 nm	$\frac{[\text{RuO}_4^-]}{\text{M} \times 10^4}$	$\frac{[\text{RuO}_4^-]}{1.806}$
30	0.502	1.724	0.955
40	0.506	1.718	.951
50	0.522	1.697	.940
70	(1.950)	1.667	.923
80	(1.938)	1.649	.913
90	0.550	1.659	.919
100	0.554	1.653	.915
120	(1.930)	1.637	.906
140	0.563	1.641	.909
160	0.566	1.637	.906
180	0.568	1.634	.905
200	0.570	1.632	.904
250	(1.910)	1.606	.889
300	0.598	1.594	.883
350	0.600	1.591	.881
400	(1.900)	1.591	.881
500	(1.893)	1.580	.875
600	0.630	1.551	.859

Table A-2

TOTAL Ru Concentration, Experiment 1

Time	Absorbance		$\frac{[\text{RuO}_4^-]}{\text{M} \times 10^4}$	$\frac{[\text{RuO}_4^-]}{\text{M} \times 10^4}$	Σ
	383.5 nm	465.0 nm			
120	1.929	0.560	1.639	0.399	2.038
250	1.910	0.580	1.610	0.426	2.036
400	1.900	0.600	1.591	0.452	2.043
510	1.893	0.615	1.577	0.471	2.048
600	1.890	0.621	1.571	0.470	2.050
					<u>2.043</u> $\pm$.006

APPENDIX A (cont'd)

Next, the experiment was repeated with 20.0 ml of $2.49 \times 10^{-4} \text{ M } \text{H}_2\text{PO}_2^-$ in place of the KOH solution (Table A3). The first experiment was then repeated (Table A5). In succeeding experiments the two solutions were alternated in the described manner. The total $\text{RuO}_4^- + \text{RuO}_4^=$ concentration was calculated from absorbances in each experiment by means of absorptivities given by Luoma¹⁶ (Tables A2, A4, and A6).

Plots of RuO_4^- concentration vs time made from data in Tables A1 and A5 indicate reduction of RuO_4^- to $\text{RuO}_4^=$. This was always observed, never eliminated, and was independent of care in cleaning vessels or care in preparation of reagents. The extent of the reduction decreased with decreasing concentration of KOH as in experiments performed to determine pH dependence. It is reasonable to conclude the KOH pellets contained a trace of oxidizable matter.

The initial $[\text{RuO}_4^-]$ (at mixing) is obtained by extrapolation of the smoothed curve of $[\text{RuO}_4^-]$ vs time from blank experiments. (A computer program written for interpolation and extrapolation²⁵ was used for this purpose. Results are listed in Table A7.) This extrapolated value was the basis for calculating the fraction of $[\text{RuO}_4^-]$

Table A-3

Absorbance at 14.7°C, Experiment 2

Time (sec)	Absorbance (383.5 nm) 465.0 nm	$\underline{M} \times 10^4$		
		$[\text{RuO}_4^-]$	$[\text{RuO}_4^-]$ Factor	$x = 1.807 - [\text{RuO}_4^-]$
30	0.890	1.243	1.293	0.514
40	0.990	1.108	1.159	0.648
50	1.080	0.986	1.047	0.760
60	1.158	0.881	0.947	0.860
70	1.223	0.793	0.854	0.953
80	1.282	0.713	0.775	1.032
90	1.320	0.662	0.720	1.087
100	1.365	0.601	0.657	1.150
120	(1.186)	0.477	0.526	1.181
140	1.514	0.399	0.441	1.366
160	1.563	0.333	0.369	1.438
180	1.602	0.281	0.312	1.495
200	1.637	0.233	0.259	1.548
250	(0.967)	0.143	0.162	1.645
300	(0.932)	0.089	0.101	1.706
350	1.769	0.055	0.063	1.794
400	1.780	0.040	0.046	1.761
500	1.805	0.006	0.007	1.800
600	1.816	0	0	1.807

Table A-4

TOTAL Ru Concentration, Experiment 1

Time	Absorbance		$[\text{RuO}_4^-]$	$\underline{M} \times 10^4$ $[\text{RuO}_4^-]$	Σ
	383.5 nm	465.0 nm			
140	1.139	1.515	0.403	1.681	2.084
230	0.981	1.680	0.168	1.906	2.074
320	0.921	1.756	0.072	2.008	2.080
480	0.882	1.802	0.012	2.070	2.082
550	0.864	1.810	0.014	2.092	2.078
					$2.080 \pm .006$

Table A-5

Absorbance at 14.7°C, Experiment 3

Time (sec)	Absorbance (383.5 nm) 465.0 nm	$\left[\text{RuO}_4^-\right]$ $\text{M} \times 10^4$	$\left[\text{RuO}_4^-\right]$ 1.809	Mean col 4 Tables A1 and A5
30	0.512	1.751	0.968	0.961
40	0.522	1.738	0.961	.956
50	0.545	1.707	.944	.942
60	(1.985)	1.698	.939	.930
70	(1.980)	1.690	.934	.929
80	(1.972)	1.678	.928	.920
90	(1.964)	1.666	.921	.920
100	(1.955)	1.652	.913	.914
120	0.594	1.640	.907	.907
140	0.600	1.632	.902	.905
160	(1.940)	1.629	.901	.903
180	(1.936)	1.623	.897	.901
200	(1.933)	1.619	.895	.899
250	0.630	1.592	.880	.885
300	(1.915)	1.591	.880	.881
350	(1.912)	1.587	.877	.879
400	0.646	1.570	.868	.874
500	(1.900)	1.568	.867	.871
600	(1.893)	1.558	.861	.845

Table A-6

TOTAL Ru Concentration, Experiment 3

Time	Absorbance		$\left[\text{RuO}_4^-\right]$	$\left[\text{RuO}_4^-\right]$ $\text{M} \times 10^4$	Σ
	383.5 nm	465.0 nm			
160	1.940	0.604	1.628	0.451	2.079
290	1.915	0.631	1.591	0.488	2.079
520	1.879	0.653	1.565	0.503	2.068
600	1.893	0.662	1.554	0.529	2.083
750	1.885	0.671	1.542	0.541	2.083

2.078 $\pm$.006

Table A-7

Extrapolated RuO_4^- Concentration at $t = 0.0$ sec.

Data from Table	<u>0</u>	<u>30</u>	<u>40</u>	<u>50</u>
A1	1.806*	1.731	1.710	1.691
A1	1.809	1.752	1.733	1.714

* $[\text{RuO}_4^-] \text{ M} \times 10^4$

APPENDIX A (cont'd)

remaining at each time t (column 4 of Tables A1 and A5 for experiments preceeding and following the H_2PO_2^- reaction. These values were averaged (Table A5, column 5) and divided into the observed $[\text{RuO}_4^-]$ for the H_2PO_2^- reaction (Table A3, column 4). The input variable x is obtained by subtracting the corrected $[\text{RuO}_4^-]$ (Table A3, column 4) from the average of the extrapolated initial $[\text{RuO}_4^-]$ (Table A7). Figure A2 is a computer plot of x (input and calculated from equation (2)) vs time for data in Table A3 with initial $[\text{RuO}_4^-] = 1.807 \times 10^{-4} \text{ M}$. If the initial $[\text{RuO}_4^-]$ is allowed to be an adjustable parameter, the calculated value is usually within 3% of the extrapolated value (Figure A3). In this case, the values of $[\text{RuO}_4^-]$ and k_2 which minimize the residuals are $1.829 \times 10^{-4} \text{ M}$ and $47.3 \text{ M}^{-1} \text{ sec}^{-1}$, respectively, as opposed to $1.807 \times 10^{-4} \text{ M}$ and $48.5 \text{ M}^{-1} \text{ sec}^{-1}$.

Figure A-2
Extent of Reaction vs Time

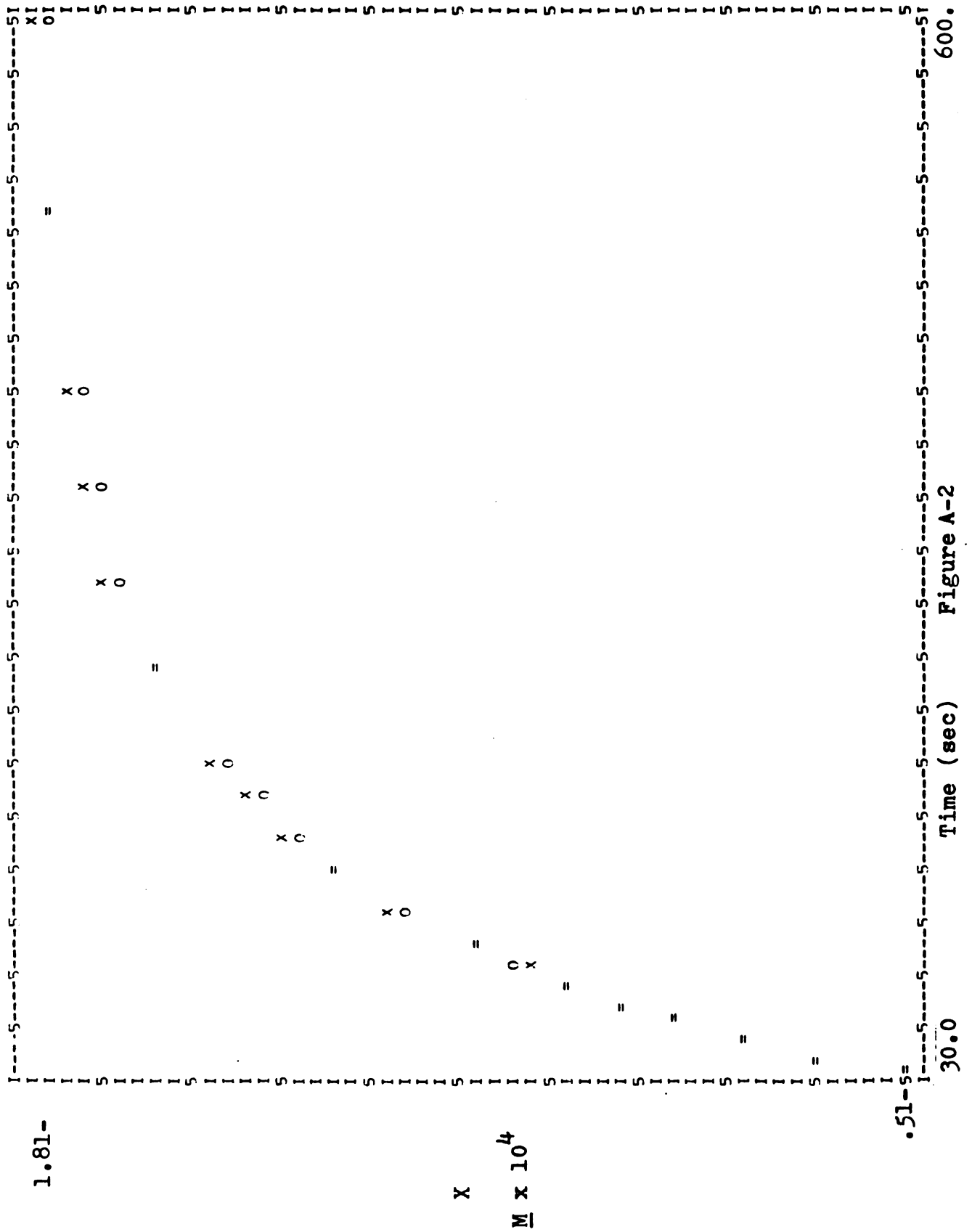
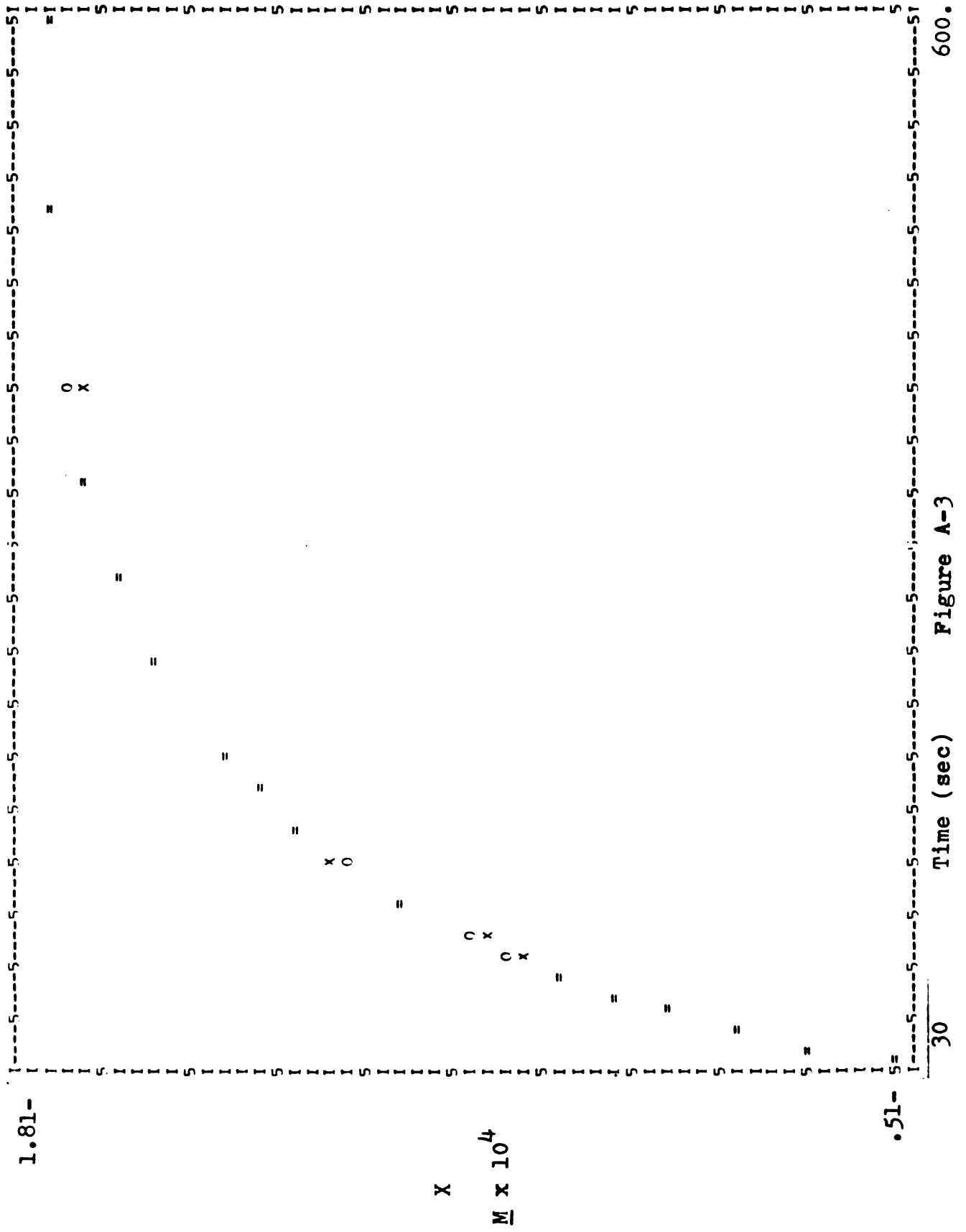


Figure A-3
Extent of Reaction vs Time, 2 Parameters



APPENDIX B
OTHER EXPERIMENTAL WORK

APPENDIX B

OTHER EXPERIMENTAL WORK

The reduction of Tl(III) by hypophosphorus acid in perchloric acid was the first project undertaken. All reagents were purified and stock solutions prepared. Before experiments were begun, the published results of Gupta and Gupta⁷ were received. The project was abandoned and efforts were redirected along other lines. It was noted that white crystals were obtained from concentrated solutions of Tl(III) and H_3PO_2 . These crystals decomposed to a yellow colored substance with a phosphine smell when they were dried.

The oxygen necessary to convert P(I) to P(III) usually originates in the solvent water. If the oxidant also has oxygen, from which source would the oxygen come? The second project was directed to this question. The search for a reducible (by hypophosphite at a measurable rate) oxocation included the following species:

URANYL ION

No change was observed in the proton nmr of H_3PO_2 after three days in a solution 0.2 M in H_3PO_2 and UO_2^+ .

APPENDIX B (cont'd)

The solution was brought to boiling and Cl_2 gas (from reduction of ClO_4^-) was liberated. Substituting NO_3^- for ClO_4^- and heating produced lower oxides of nitrogen. Finally, peroxouranyl (UO_4) was dissolved in HCL solution and heated to form UO_2^{2+} . After adding H_3PO_2 , the solution was purged of oxygen and allowed to reflux overnight. Again, no change in H_3PO_2 concentration was observed in the proton nmr. Yellow plates precipitated from concentrated (about 1 M) solutions of UO_2^{2+} and H_3PO_2 .

VANADYL ION

A color change (blue to green) was observed when solutions of VO^{2+} and H_3PO_2 were mixed. Cooper¹² reported this to be a complex formation rather than a redox reaction.

PEROXOTITANYL

This yellow colored oxocation (TiO_2^{2+}) was not noticeably reduced in 24 hours at room temperature. The study was not thorough and should be reinvestigated.

SODIUM PERRUTHENATE

A substantial amount of data were collected with the sodium salts of hypophosphite and perruthenate. These data were seldom reproducible. It is likely the problem originated

APPENDIX B (cont'd)

in the preparation of NaRuO_4 . When RuO_4 is generated from NaBiO_3 and RuCl_3 , Cl^- is also oxidized to Cl_2 . When this dissolves in alkali hypochlorite, OCl^- , is produced. This powerful oxidant oxidizes $\text{RuO}_4^{=}$ to RuO_4^- and RuO_4 . (In at least one experiment RuO_4^- was reduced by H_2PO_2^- to $\text{RuO}_4^{=}$ which was oxidized back to RuO_4^- , all within 20 minutes.) Several attempts to crystallize NaRuO_4 were unsuccessful.

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